

NOTE

REACTION OF CHLORINE WITH DODECAMETHYLCYCLOHEXASILANE

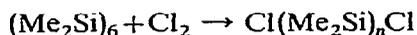
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The production of cyclic polysilanes¹ such as octaphenylcyclotetrasilane², decaphenylcyclopentasilane³ and dodecamethylcyclohexasilane⁴⁻⁶ in high yields has prompted a study on the preparation of compounds of the general formula $\text{Cl}(\text{R}_2\text{Si})_n\text{Cl}$ (where $n=2-6$).

α,ω -Dichloroperphenylpolysilanes (where $n=2-5$) have been made by the reaction of chlorinating agents such as *sym*-tetrachloroethane, chlorine and phosphorus pentachloride with octaphenylcyclotetrasilane or decaphenylcyclopentasilane⁷. Few references, however, are available concerning the corresponding α,ω -dichloropermethylpolysilanes. Kumada and co-workers, in some elegant studies, have prepared 1,2-dichloro-1,1,2,2-tetramethyldisilane⁸ (I) and 1,3-dichloro-1,1,2,2,3,3-hexamethyltrisilane⁹ from hexamethyldisilane and octamethyltrisilane, respectively, by the sulfuric acid-ammonium chloride reaction. In recent work from these laboratories it has been shown that α,ω -dichloropermethylated polysilanes can be obtained by the interaction of dodecamethylcyclohexasilane with phosphorus pentachloride in *sym*-tetrachloroethane¹⁰. In an extension of this work we have examined an improved procedure for the preparation of these dichloro compounds by the reaction of chlorine with dodecamethylcyclohexasilane.



From this reaction one can obtain the dichloro compounds where $n=2, 3, 4$, or 6 ; however, it appears that no significant amount of the homolog where $n=5$; namely, 1,5-dichlorododecamethylpentasilane, is obtained. The yields of the homologs can be varied by appropriate alterations in experimental conditions, and yields as high as 52% of (I) have been obtained.

There appears to be a significant difference between the behaviour of perphenylated cyclic polysilanes and permethylated cyclic polysilanes in their reaction with chlorinating agents¹ and particularly with chlorine⁷. The perphenylated compounds tend to cleave more easily than their aliphatic counterparts but the straight chain polysilanes produced seem to be more resistant to cleavage as is shown by the 78 and 96% yields of 1,4-dichlorooctaphenyltetrasilane and 1,5-dichlorodecaphenyl-

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pentasilane produced by the reaction of octaphenylcyclotetrasilane and decaphenylcyclopentasilane, respectively, with chlorine. In agreement with this observation the reaction of dodecamethylcyclohexasilane with chlorine often leaves some unaltered starting material but also gives dichlorodimethylsilane under some conditions. It does not appear necessary for preparative purposes to use pure dodecamethylcyclohexasilane as the less pure material seems to give equally good yields.

In connection with the above reaction we have obtained a 42.7% yield of (I) from the chlorination of the insoluble dimethylsilylene polymer $(\text{Me}_2\text{Si})_n$ (where n has an average of 55) first described by Burkhard⁴.

Some of the dichloro compounds were characterized by treatment with phenylmagnesium bromide to give the corresponding α,ω -diphenylpermethylated polysilane in high yields (comparisons with authentic samples prepared by the phosphorus pentachloride procedure described previously)¹⁰.

EXPERIMENTAL

The dodecamethylcyclohexasilane was prepared by the interaction of lithium and dichlorodimethylsilane in tetrahydrofuran (THF)⁶. All reactions were carried out in dry glassware under an atmosphere of dry oxygen-free nitrogen. Solvents used were freshly distilled or stored over sodium wire where applicable. All temperatures reported are uncorrected.

Reaction of dodecamethylcyclohexasilane with chlorine. In a general reaction pattern, dodecamethylcyclohexasilane (15.0 g, 0.043 mole) was dissolved in 100 ml of a solvent such as carbon tetrachloride, benzene, ether or carbon tetrachloride-ether mixture (1 : 1) in a 250 ml round-bottomed flask. Chlorine gas was passed, via a sintered glass gas diffusion tube, at a constant rate into the rapidly stirred solution for the required time. The reaction was quenched by the rapid removal of excess chlorine under reduced pressure and the products isolated by fractional distillation using a 12 cm Vigreux column.

In a typical experiment using carbon tetrachloride as solvent, chlorine was passed in for 15 min (190 ml/min). During the initial phase of the reaction the temperature of the system was held at -20° , later the system temperature was lowered to -30° to -40° . After removal of the chlorine the solvent was distilled off; the distillate so produced fumed in moist air and presumably contained some dichlorodimethylsilane. Fractional distillation of the residual oil gave a first fraction (8.1 g, 33.4%) of (I) b.p. $148-149^\circ$, n_D^{20} 1.4545 (lit. value for (I)⁸, b.p. 148° , n_D^{20} 1.4545); 1,3-dichlorohexamethyltrisilane (3 g, 14%) b.p. $88-90^\circ/14$ mm, n_D^{20} 1.4850, (lit. value⁸ b.p. $82-83^\circ/11$ mm, n_D^{20} 1.4852); and a third fraction containing 1,4-dichlorooctamethyltetrasilane (5 g, 25.3%) b.p. $130-132^\circ/15$ mm, n_D^{20} 1.5030. (Found: Cl, 23.50, 23.48%. $\text{C}_8\text{H}_{24}\text{Si}_4\text{Cl}_2$, calcd.: Cl, 23.20%.)

Under similar conditions passage of chlorine for 10 minutes gave 1,6-dichlorododecamethylhexasilane (5.4 g, 30%) b.p. $108-109^\circ/0.07$ mm as a low-melting solid. (Found: Cl, 16.9, 16.7%. $\text{C}_{12}\text{H}_{36}\text{Si}_6\text{Cl}_2$ calcd.: Cl, 16.87%.)

The results of this series of reactions are shown in Table 1, yields being based on the initial $-\text{Me}_2\text{Si}-$ units used.

Similar results were obtained when chlorine was passed into a solution of

TABLE I
INTERACTION OF CHLORINE AND DODECAMETHYLCYCLOHEXASILANE (II)

Solvent	Time (min)	Temp. of system (°C)	Products				
			Recovered (II) (g)	Dichloro derivatives (%)			
				1,2	1,3	1,4	1,6
CCl ₄	5	-20	26.6	trace	trace	8	27.6
CCl ₄	10	-20	20	4	trace	8	30
CCl ₄	15	-20	—	33.4	13	25.3	—
CCl ₄	20	-20	—	40	8	trace	—
CCl ₄	25	-20	—	50	—	—	—
CCl ₄	30	-20	—	50	—	—	—
CCl ₄	35	-20	—	50.8	—	—	—
CCl ₄	60	-20	—	24.8	—	—	—
CCl ₄	10	0 to -10	13	9.9	8.5	13.1	22
CCl ₄	10	0 ± 2	trace	10.3	5.2	16.7	23.8
CCl ₄	10	5 to 8	trace	8.1	9.3	20.2	24.9
CCl ₄	10	15 to 20	—	14.8	19.4	18.2	—
Ether	30	-20	—	37.5	—	—	—
Ether:CCl ₄ (1:1)	35	-20	—	52	—	—	—
Benzene	35	0 ± 5	—	47.5	—	—	—

"crude" dodecamethylcyclohexasilane (free of moisture and insoluble polymer but containing some unidentified polymethylsilanes) in carbon tetrachloride under similar conditions at -20° ; in general greater reaction time gave higher yields of (I) and correspondingly lower yields of higher polysilanes than a shorter reaction time. After passage of chlorine for 70 min a 50% yield of (I) was obtained as the only isolable product.

Reaction of dimethylsilylene polymer with chlorine. In a similar manner dry chlorine gas was passed (190 ml/min) into a stirred suspension of the polymer^{1,4} (14.52 g, 0.25 mole of $-\text{SiMe}_2-$) in carbon tetrachloride (100 ml) at -20° for varying lengths of time. After passing chlorine for 35 mins all the suspended solid went into solution.

TABLE 2
INTERACTION OF DIMETHYLSILYLENE POLYMER WITH CHLORINE

Time (min)	Yield of (I) (%)
30	38.4
35	42.7
45	20
60	17

Derivatization of 1,4-dichlorooctamethyltetrasilane with phenylmagnesium bromide. 1,4-Dichlorooctamethyltetrasilane (3.03 g, 0.01 mole) dissolved in THF (40 ml) was added slowly, with stirring, to a solution of phenylmagnesium bromide (0.06 mole) in THF. Subsequent work-up gave 1,4-diphenyloctamethyltetrasilane (2 g, 50% yield) m.p. $60-62^{\circ}$, (reported¹⁰ m.p. $61-63^{\circ}$) identified by mixed m.p. and infrared spectra.

Derivatization of 1,6-dichlorododecamethylhexasilane with phenylmagnesium bromide. 1,6-Dichlorododecamethylhexasilane (3.18 g, 0.0076 mole) in THF (30 ml) was added slowly to a stirred solution of phenylmagnesium bromide (0.05 mole) in THF (50 ml). The customary work-up gave 1,6-diphenyldodecamethylhexasilane (2.8 g, 90% yield) m.p. 85–87° (after recrystallization from methanol) (lit.¹⁰ m.p. 86–87°) identified by mixed m.p. and infrared spectra.

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